

The Mayer series of the Lennard-Jones gas: improved bounds for the convergence radius

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Abstract

We provide a lower bound for the convergence radius of the Mayer series of the Lennard-Jones gas which strongly improves on the classical bound obtained by Penrose and Ruelle 1963. To obtain this result we use an alternative estimate recently proposed by Morais et al. (J. Stat. Phys. 2014) for a restricted class of stable and tempered pair potentials (namely those which can be written as the sum of a non-negative potential plus an absolutely integrable and stable potential) combined with a method developed by Locatelli and Schoen (J. Glob. Optim. 2002) for establishing a lower bound for the minimal interatomic distance between particles interacting via a Morse potential in a cluster of minimum-energy configurations.

1 Introduction

In this note we will consider a system of classical particles interacting via a Lennard-Jones pair potential V_{LJ} (see definition ahead, formula (2.12)). Such a system is considered as a topical model for a monoatomic or molecular gas of particles in statistical mechanics and the literature about it is huge. The rigorous approach to this system has been done mainly in the grand-canonical ensemble. In this ensemble it is possible to prove that the pressure of the gas, which is proportional to the logarithm of the grand partition function divided by the volume, is an analytic function of the particle fugacity λ as long as $\lambda \in \mathbb{C}$ is inside a disk of radius R depending on the inverse temperature β (and going to ∞ as $\beta \rightarrow 0$) uniformly in the volume. This result is physically interpreted by saying that for such values of λ inside the convergence region there are no phase transitions and the system is in the pure gas phase. The best estimate for the convergence radius of the pressure series for such systems dates back to the sixties and has been given independently by Penrose [11, 12] and Ruelle [17, 18]. Actually, the Penrose-Ruelle estimate works for a wide class of pair potentials, i.e. stable and tempered pair potential, which of course includes the Lennard-Jones pair potential. Improvements on the Penrose-Ruelle bound have been recently given for some specific cases of stable and tempered pair potentials: namely, for purely hard core gases [3] and for gases interacting via hard-core potentials with an attractive tail [10, 13, 14, 15]. In particular, an alternative estimate of the same convergence radius has been proposed in [10] for a restricted class of stable and tempered pair potentials (namely those which can be written as the sum of a non-negative potential plus an absolutely integrable and stable potential) which still includes the Lennard-Jones potential. However, no explicit calculations for the Lennard-Jones potential are presented in [10] due to the difficulty in evaluating the stability constant of the absolutely summable part of the splitting of the pair potential.

In the present paper we overcome this difficulty showing that it is indeed possible to split the Lennard-Jones potential as described above in such a way that the stability constant of the absolutely integrable part of the splitting is exactly equal to the stability constant of the whole Lennard-Jones potential. To obtain this result we use a method developed by Locatelli and Schoen in 2002 [6] for establishing a lower bound for the minimal interatomic distance between particles interacting via a Morse potential (see e.g. [1, 10, 19] for the definition) in a cluster of minimal-energy configurations. The extension of the Locatelli-Schoen technique to the cut-off Lennard-Jones pair potential will permit us to efficiently use the new estimate proposed in [10] in such a way that we obtain a lower bound for the convergence radius of the Lennard-Jones gas which strongly improves the classical one obtained by Ruelle and Penrose in 1963.

The rest of this paper is organized as follows. In Section 2 we will introduce notations and the model. We further present our main results in the form of a technical lemma (Lemma 1) and, as an immediate corollary of this lemma, the improvement on the classical bound (Theorem 3). Finally in Section 3 we present the proof of Lemma 1 and conclude this section by briefly discussing possible generalizations.

2 Notations and Results

Throughout the paper, if S is a set, then $|S|$ denotes its cardinality. If $n \in \mathbb{N}$ is a natural number then we will denote shortly $I_n = \{1, 2, \dots, n\}$. We also denote by $\mathbb{Z}^+ = \mathbb{N} \cup \{0\} = \{0, 1, 2, \dots\}$ the set of non-negative integers. We will focus our attention on a system of classical, identical particles in \mathbb{R}^3 (generally enclosed in a cubic box $\Lambda \subset \mathbb{R}^3$ with volume $|\Lambda|$). We denote by $x_i \in \mathbb{R}^3$ the position vector of the i^{th} particle and by $|x_i|$ its modulus. We will further assume that these particles interact through a translational and rotational invariant, stable and tempered pair potential $V(|x_i - x_j|)$, so that, given N particles in positions $(x_1, \dots, x_N) \in \Lambda^N$, their configurational energy $U(x_1, \dots, x_N)$ is

$$U(x_1, \dots, x_N) \doteq \sum_{1 \leq i < j \leq N} V(|x_i - x_j|)$$

We recall that a pair potential $V(|x_i - x_j|)$ is said to be *stable* (see e.g. [16]) if there exists a constant $B \geq 0$ such that the configurational energy of the N particles in the positions $(x_1, \dots, x_N) \in \Lambda^N$ satisfies, for all $N \in \mathbb{N}$ and $(x_1, \dots, x_N) \in \mathbb{R}^{3N}$

$$U(x_1, \dots, x_N) \geq -BN$$

We also remind the reader that a pair potential $V(|x|)$ is said to be *tempered* (see again [16]) if there exists a constant $r_0 \geq 0$ such that

$$\int_{|x| \geq r_0} |V(|x|)| dx < +\infty \quad (2.1)$$

Moreover, as a consequence of stability and temperedness it is easy to check that, for all $\beta > 0$

$$C(\beta) \doteq \int_{\mathbb{R}^3} |e^{-\beta V(|x|)} - 1| dx < +\infty \quad (2.2)$$

The grand canonical partition function $\Xi_\Lambda(\beta, \lambda)$ of the system is given by

$$\Xi_\Lambda(\beta, \lambda) = 1 + |\Lambda|\lambda + \sum_{N \geq 2} \frac{\lambda^N}{N!} \int_\Lambda \dots \int_\Lambda e^{-\beta \sum_{1 \leq i < j \leq N} V(|x_i - x_j|)} dx_1 \dots dx_N \quad (2.3)$$

with $\beta > 0$ being the inverse temperature, and $\lambda > 0$ being the fugacity. The pressure of the system is given by

$$P(\beta, \lambda) = \lim_{|\Lambda| \rightarrow \infty} \frac{1}{\beta|\Lambda|} \log \Xi_\Lambda(\beta, \lambda) \quad (2.4)$$

The limit (2.4) is known to exist whenever the pair potential $V(|x|)$ is stable and tempered (see e.g. [16], sections 3.3 and 3.4). Moreover, a very well known and old result (see e.g. [7, 8, 9, 16]) states that the factor $\log \Xi_\Lambda(\beta, \lambda)$ can be written in terms of a formal series in power of λ . Namely,

$$\frac{1}{|\Lambda|} \log \Xi_\Lambda(\beta, \lambda) = \sum_{n \geq 1} C_n(\beta, \Lambda) \lambda^n \quad (2.5)$$

where $C_1(\beta, \Lambda) = 1$ and, for $n \geq 2$,

$$C_n(\beta, \Lambda) = \frac{1}{|\Lambda|} \frac{1}{n!} \int_\Lambda \cdots \int_\Lambda \sum_{g \in G_n} \prod_{\{i,j\} \in E_g} \left[e^{-\beta V(|x_i - x_j|)} - 1 \right] dx_1 \dots dx_n \quad (2.6)$$

with G_n being the set of all connected graphs with vertex set I_n and E_g denoting the edge-set of a graph $g \in G_n$. The series (2.5) is known to converge absolutely for λ sufficiently small (uniformly in the volume $|\Lambda|$) as long as the pair potential $V(|x|)$ is stable and tempered. The best rigorous bound on $|C_n(\beta, \Lambda)|$ (and consequently on the convergence radius of the series (2.5)) to date is the one obtained by Penrose and (independently) by Ruelle in 1963.

Theorem 1 (Penrose-Ruelle) *Let $V(|x|)$ be a stable and tempered pair potential. Let B be its stability constant. Then the n -th order Mayer coefficient $C_n(\beta, \Lambda)$ defined in (2.6) admits the bound*

$$|C_n(\beta, \Lambda)| \leq e^{2\beta B(n-1)} n^{n-2} \frac{[C(\beta)]^{n-1}}{n!} \quad (2.7)$$

where $C(\beta)$ is the function defined in (2.2).

Consequently, the Mayer series in the r.h.s. of (2.5) converges absolutely, uniformly in Λ , for any complex λ inside the disk

$$|\lambda| < \frac{1}{e^{2\beta B+1} C(\beta)} \quad (2.8)$$

As said in the introduction, Morais et al. [10] proposed a new bound which can be used in place of the the Penrose-Ruelle bound when the pair potentials can be written as the sum of non-negative tempered part plus an absolutely summable stable part.

Theorem 2 (Morais-Procacci-Scoppola) *Let $V(|x|) = \Phi_1(|x|) + \Phi_2(|x|)$ be a pair potential such that $\Phi_1(|x|)$ is non-negative and tempered and $\Phi_2(|x|)$ absolutely summable and stable. Let \tilde{B} the stability constant of the potential $\Phi_2(|x|)$. Then n -th order Mayer coefficient $C_n(\beta, \Lambda)$ defined in (2.6) admits the bound*

$$|C_n(\beta, \Lambda)| \leq e^{\beta \tilde{B}n} n^{n-2} \frac{[\tilde{C}(\beta)]^{n-1}}{n!} \quad (2.9)$$

where

$$\tilde{C}(\beta) = \int_{\mathbb{R}^3} \left[|e^{-\beta \Phi_1(|x|)} - 1| + \beta |\Phi_2(|x|)| \right] dx \quad (2.10)$$

Consequently, the Mayer series converges absolutely for all complex activities λ such that

$$|\lambda| < \frac{1}{e^{\beta\tilde{B}+1}\tilde{C}(\beta)} \quad (2.11)$$

In this note we will focus our attention to the Lennard-Jones pair potential $V_{\text{LJ}}(|x|)$. The standard definition in the literature is as follows.

$$V_{\text{LJ}}(|x|) = \frac{1}{|x|^{12}} - \frac{2}{|x|^6} \quad (2.12)$$

Note that the Lennard-Jones potential $V_{\text{LJ}}(|x|)$ defined in (2.12) is positive for $|x| < 2^{-1/6}$, negative for $|x| > 2^{-1/6}$ and reaches its minimum at $|x| = 1$ where it takes the value -1. It is well known that $V_{\text{LJ}}(|x|)$ is stable and tempered (see e.g. [4, 5, 16], i.e. it belongs to the class of pair potentials which satisfy Theorem 1. Let us denote by B_{LJ} its stability constant. In other words B_{LJ} is the (minimal) constant such that, for all $N \in \mathbb{N}$ and $(x_i, \dots, x_N) \in \mathbb{R}^{3N}$

$$\sum_{1 \leq i < j \leq N} V_{\text{LJ}}(|x_i - x_j|) \geq -B_{\text{LJ}}N \quad (2.13)$$

On the other hand, in [10] it has also been shown that $V_{\text{LJ}}(|x|)$ belongs to the class of pair potentials satisfying Theorem 2 so that one could also use (2.9)-(2.11) to get an estimate of the convergence radius. The problem is that the stability constant of the absolutely summable part of the pair potential appearing in (2.11), being in principle different (and possibly bigger) than the stability constant B appearing in bound (2.8), appears to be quite difficult to be estimated efficiently.

In this paper we overcome the difficulties concerning the application of bound (2.11) to the specific case of the Lennard-Jones potential and we show that it is possible to write $V_{\text{LJ}}(|x|)$ as a sum of a non-negative tempered part plus an absolutely summable stable part whose stability constant is the same constant B_{LJ} of the whole Lennard-Jones potential. More precisely, we prove the following Lemma

Lemma 1 *There exists $a \in (0, 2^{-1/6})$ such that, defining*

$$V_a(|x|) = \begin{cases} \frac{1}{|x|^{12}} - \frac{2}{|x|^6}, & \text{if } |x| > a \\ \frac{1}{a^{12}} - \frac{2}{a^6}, & \text{if } |x| \leq a \end{cases} \quad (2.14)$$

the potential $V_a(|x|)$ is stable with stability constant equal to the stability constant of the whole Lennard-Jones potential $V(|x|)$ defined in (2.12).

This Lemma, whose proof will be given in the next section, yields straightforwardly new bounds for the convergence radius of the Mayer series of the Lennard-Jones gas which strongly improve the classical Penrose-Ruelle bound. Indeed, by writing $V_{\text{LJ}}(|x|) = \Phi_1(|x|) + \Phi_2(|x|)$ with $\Phi_1(|x|) = V_{\text{LJ}}(|x|) - V_a(|x|)$, $\Phi_2(|x|) = V_a(|x|)$ and choosing the constant a in such way that Lemma 1 is satisfied, we immediately get the following theorem, which is the main result of this note.

Theorem 3 *Let $V_{\text{LJ}}(|x|)$ as in (2.12). Then there exists $a \in (0, 2^{-\frac{1}{6}})$ such that the n -th order Mayer coefficient $C_n(\beta, \Lambda)$ defined in (2.6) admits the bound*

$$|C_n(\beta, \Lambda)| \leq e^{\beta B_{\text{LJ}} n} n^{n-2} \frac{[\tilde{C}(\beta)]^{n-1}}{n!} \quad (2.15)$$

where

$$\tilde{C}(\beta) = \int_{\mathbb{R}^3} \left[|e^{-\beta[V_{\text{LJ}}(|x|) - V_a(|x|)]} - 1| + \beta |V_a(|x|)| \right] dx \quad (2.16)$$

Consequently, the Mayer series of the Lennard-Jones gas absolutely converges for all complex activities λ such that

$$|\lambda| < \frac{1}{e^{\beta B_{\text{LJ}} + 1} \tilde{C}(\beta)} \quad (2.17)$$

By (2.16) it is clear that the larger is a , the smaller is the factor $\tilde{C}(\beta)$ and consequently the larger is the lower bound for the convergence radius given by (2.17). We did not try to optimize a , however, as shown in the next section, one can take $a = 0.3637$ in order to satisfy Lemma 1.

We conclude this section by giving an idea about how Theorem 3 above improves the classical bound of Theorem 1. Putting $\beta = 1$ for the sake of simplicity let us denote shortly $\rho_{\text{PR}} = 1/(e^{2B+1}C(\beta=1))$ the Penrose-Ruelle estimate (2.8) for the convergence radius and let $\rho_{\text{new}} = 1/(e^{B+1}\tilde{C}(\beta=1))$ be our new estimate (2.17) for same the convergence radius. Observe now that the factor $\tilde{C}(\beta=1)$ appearing in the denominator of the r.h.s. of (2.17) is surely smaller than 50000. Indeed one can check that

$$\tilde{C}(\beta=1) \leq \frac{4}{3}\pi(0.3637)^3 [1 + (0.3637)^{-12}] + 4\pi \int_{0.3637}^{\infty} \left| \frac{1}{r^{12}} - \frac{2}{r^6} \right| r^2 dr < 50000$$

So that we surely can say that

$$\rho_{\text{new}} > \frac{e^{-B_{\text{LJ}}}}{50000}$$

On the other hand the factor $C(\beta=1)$ appearing in the classical bound (2.8) is surely larger than 7.89. Indeed it is immediate to check that

$$C(\beta=1) \geq 4\pi \int_{2^{-1/6}}^{\infty} \left| \frac{1}{r^{12}} - \frac{2}{r^6} \right| r^2 dr > 7.89$$

whence we have that

$$\rho_{\text{PR}} < \frac{e^{-2B_{\text{LJ}}}}{7.89}$$

Thus the ratio $\rho_{\text{new}}/\rho_{\text{PR}}$ between the new estimate (2.17) for the convergence radius and the old estimate (2.8) for the same convergence radius is surely larger than

$$\frac{\rho_{\text{new}}}{\rho_{\text{PR}}} > e^{B_{\text{LJ}}} \frac{7.89}{50000} \geq \frac{e^{B_{\text{LJ}}}}{6338}$$

The best estimate (from above) for the stability constant B_{LJ} of the Lennard-Jones potential is, as far as we know, the one recently obtained in [19]. Namely, $B_{\text{LJ}} \leq 41.66$. Using this estimate we have that our new bound for the convergence radius based on (2.11) is, at inverse temperature $\beta = 1$, at least $e^{32.9}$ times large than bound (2.8).

3 Proof of Lemma 1

Let $a \in (0, 2^{-1/6})$ and let $V_a(|x|)$ as in (2.14). Given a configuration (x_1, \dots, x_N) of particles we denote by

$$U_a(x_1, \dots, x_N) = \sum_{1 \leq i < j \leq N} V_a(|x_i - x_j|)$$

the energy of such configuration. We also denote (shortly)

$$W_a(i, \mathbf{x}_N) = \sum_{\substack{j \in I_N \\ j \neq i}} V_a(|x_i - x_j|)$$

and note that

$$U_a(x_1, \dots, x_N) = \frac{1}{2} \sum_{i \in I_N} W_a(i, \mathbf{x}_N)$$

Let now $\mathbf{x}_N^* \doteq (x_1^*, \dots, x_N^*)$ be a minimum-energy configuration for the pair potential $V_a(|x|)$, i.e. (x_1^*, \dots, x_N^*) is such that

$$U_a(x_1^*, \dots, x_N^*) \leq U_a(x_1, \dots, x_N) \quad \forall (x_1, \dots, x_N) \in \mathbb{R}^{3N}$$

We define

$$r_{\min}^a(\mathbf{x}_N^*) = \min_{\{i, j\} \subset I_N} |x_i^* - x_j^*|$$

We denote by \mathbb{U}_N^a the set of all minimum-energy configurations of N particles interacting via the pair potential $V_a(|x|)$.

Proposition 1 *If $\mathbf{x}_N^* = (x_1^*, \dots, x_N^*) \in \mathbb{U}_N^a$ then*

$$W_a(i, \mathbf{x}_N^*) < 0, \quad \forall i \in I_N$$

Proof. Suppose by contradiction that $(x_1^*, \dots, x_N^*) \in \mathbb{R}^{3N}$ is a minimum-energy configuration but $W_a(i, N) \geq 0$. Then we can move the particle i from x_i^* to the position x_i sufficiently far from (the convex hull of) the other particles in such way that $W_a(i, N) < 0$ (recall that $V_a(|x|) < 0$ as soon as $|x| > 2^{-1/6}$). This new configuration $(x_1^*, \dots, x_i, \dots, x_N^*)$ has thus energy less than the energy of the minimum-energy configuration (x_1^*, \dots, x_N^*) which is a contradiction. \square

Let now, for $(x_1^*, \dots, x_N^*) \in \mathbb{U}_N^a$

$$W_a^+(i, \mathbf{x}_N^*) = \sum_{\substack{j \in I_N: j \neq i \\ |x_i^* - x_j^*| < 2^{-1/6}}} V_a(|x_i^* - x_j^*|)$$

$$W_a^-(i, \mathbf{x}_N^*) = \sum_{\substack{j \in I_N: j \neq i \\ |x_i^* - x_j^*| \geq 2^{-1/6}}} V_a(|x_i^* - x_j^*|)$$

So that

$$W_a(i, \mathbf{x}_N^*) = W_a^+(i, \mathbf{x}_N^*) + W_a^-(i, \mathbf{x}_N^*)$$

with $W_a^+(i, \mathbf{x}_N^*) > 0$ and $W_a^-(i, \mathbf{x}_N^*) \leq 0$. Let now define

$$W_a^+(\mathbf{x}_N^*) = \max_{i \in I_N} W_a^+(i, \mathbf{x}_N^*)$$

Clearly, for $\mathbf{x}_N^* \in \mathbb{U}_N^a$ we have that

$$W_a^+(\mathbf{x}_N^*) \geq V_a(r_{\min}(\mathbf{x}_N^*)) \quad (3.1)$$

Indeed, let $k, l \in I_N$ such that $|x_k^* - x_l^*| = r_{\min}(\mathbf{x}_N^*)$. Then $W_a^+(\mathbf{x}_N^*) \geq W^+(k, \mathbf{x}_N^*) \geq V_a(r_{\min}(\mathbf{x}_N^*))$.

Without loss of generality we assume that the particle with index $i = 1$ is such that $W_a^+(\mathbf{x}_N^*) = W_a^+(1, \mathbf{x}_N^*)$ and we also suppose, again without loss of generality, that this particle is in the origin, i.e. $x_1^* = 0$. Let now consider, for $n \in \mathbb{N}$, spheres $S_n = \{x \in \mathbb{R}^3 : |x| \leq 2n\}$ with center in $x_1^* = 0$ and radius $2n$ and observe that

$$\text{Vol}(S_n) = \text{Vol}(S_1)n^3$$

Let us now define, for $\mathbf{x}_N^* \in \mathbb{U}_N^a$,

$$d_n(\mathbf{x}_N^*) = \frac{|\{i \in I_N : x_i^* \in S_n\}|}{\text{Vol}(S_n)}$$

and let

$$d(\mathbf{x}_N^*) = \max_{n \geq 1} d_n(\mathbf{x}_N^*)$$

Proposition 2 *Let $\mathbf{x}_N^* \in \mathbb{U}_N^a$, then there exist a $c_0 \in (0, 1)$ such that*

$$d(\mathbf{x}_N^*) \geq c_0 \frac{W_a^+(\mathbf{x}_N^*)}{\text{Vol}(S_1)}$$

Proof. First let us recall that, in view of Proposition 1, we have that

$$W_a(1, \mathbf{x}_N^*) = W_a^+(\mathbf{x}_N^*) + W_a^-(1, \mathbf{x}_N^*) < 0$$

and thus

$$W_a^-(1, \mathbf{x}_N^*) < -W_a^+(\mathbf{x}_N^*) \quad (3.2)$$

Let now, for any $n \in \mathbb{N}$ (put $S_0 = \emptyset$ by convention)

$$\text{Sol}_n = \{i \in I_N : x_i^* \in S_n \setminus S_{n-1}\}$$

In other words, Sol_n is the set of indices in I_N carried by the particles of the minimum-energy configuration \mathbf{x}_N^* which lay between spheres S_n and S_{n-1} . Then we have (recall that, for $|x| \geq a$ we have that $V_a(|x|) = \frac{1}{|x|^{12}} - \frac{2}{|x|^6}$ and the latter is decreasing for $|x| \geq 1$)

$$W_a^-(1, \mathbf{x}_N^*) \geq -|\text{Sol}_1| + \sum_{n=2}^{\infty} \left[\frac{1}{(2n-2)^{12}} - \frac{2}{(2n-2)^6} \right] |\text{Sol}_n|$$

Let us first suppose that there exists $n_0 \geq 2$ such that

$$|\text{Sol}_{n_0}| \geq n_0^3 W_a^+(\mathbf{x}_N^*)$$

then the proposition follows since

$$d(\mathbf{x}_N^*) \geq d_{n_0}(\mathbf{x}_N^*) = \frac{|\cup_{n=1}^{n_0} Sol_n|}{\text{Vol}(S_{n_0})} \geq \frac{|Sol_{n_0}|}{n_0^3 \text{Vol}(S_1)} \geq \frac{W_a^+(\mathbf{x}_N^*)}{\text{Vol}(S_1)} \geq c_0 \frac{W_a^+(\mathbf{x}_N^*)}{\text{Vol}(S_1)}, \forall c_0 \in (0, 1)$$

Let us thus suppose that

$$|Sol_n| < n^3 W_a^+(\mathbf{x}_N^*) \quad \text{for all } n \geq 2$$

Then

$$\begin{aligned} W_a^-(1, \mathbf{x}_N^*) &\geq -|Sol_1| + W_a^+(\mathbf{x}_N^*) \sum_{n=2}^{\infty} \left[\frac{1}{(2n-2)^{12}} - \frac{2}{(2n-2)^6} \right] n^3 \geq \\ &\geq -|Sol_1| - \frac{W_a^+(\mathbf{x}_N^*)}{32} \sum_{n=2}^{\infty} \frac{n^3}{(n-1)^6} \end{aligned}$$

We now bound

$$\sum_{n=2}^{\infty} \frac{n^3}{(n-1)^6} \leq 8 + \frac{3^3}{2^6} + \frac{4^3}{3^6} + \int_4^{\infty} \frac{x^3}{(x-1)^6} dx < 9$$

Hence

$$W_a^-(1, \mathbf{x}_N^*) \geq -|Sol_1| - \frac{9}{32} W_a^+(\mathbf{x}_N^*)$$

and recalling (3.2) we get

$$W_a^+(\mathbf{x}_N^*) \leq |Sol_1| + \frac{9}{32} W_a^+(\mathbf{x}_N^*)$$

i.e.

$$|Sol_1| \geq \frac{23}{32} W_a^+(\mathbf{x}_N^*)$$

Observing now that $|Sol_1| = \text{Vol}(1) d_1(\mathbf{x}_N)$ we get that

$$d_1(\mathbf{x}_N) \geq \frac{23}{32} \frac{W_a^+(\mathbf{x}_N^*)}{\text{Vol}(1)}$$

and the proposition follows by the fact that $d(\mathbf{x}_N) \geq d_1(\mathbf{x}_N)$ and we get

$$c_0 \geq \frac{23}{32} \tag{3.3}$$

□

Let us now divide \mathbb{R}^3 into elementary cubes Δ of size ℓ such that

$$\sqrt{3}\ell < 2^{-1/6} \tag{3.4}$$

We suppose that these cubes Δ are half-open and half closed in an arbitrary way, such that they are disjoint, i.e. $\Delta \cap \Delta' = \emptyset$ if $\Delta \neq \Delta'$, and their union is \mathbb{R}^3 . Let us denote by $\Omega_n(\ell)$ the number of elementary cubes necessary to cover S_n . An upper bound for $\Omega_n(\ell)$ is

$$\Omega_n(\ell) \leq \bar{\Omega}_n(\ell) \doteq \left(\frac{4}{\ell}\right)^3 n^3 \quad (3.5)$$

The bound follows by considering that there is a cube of size $4n$ which contains the sphere S_n and this cube contains at most $\lceil (4n/\ell) \rceil^3$ elementary cubes which cover S_n . Observe that

$$\bar{\Omega}_n(\ell) = \bar{\Omega}_1(\ell)n^3$$

Proposition 3 *For $\mathbf{x}_N^* \in \mathbb{U}_N^a$, there exists at least one elementary cube Δ containing not less than*

$$\beta = \left\lceil c_0 \frac{W_a^+(\mathbf{x}_N^*)}{|\bar{\Omega}_1(\ell)|} \right\rceil \quad (3.6)$$

particles of the minimum-energy configuration \mathbf{x}_N^ .*

Proof. Let n_0 be the integer for which $d_n(\mathbf{x}_N^*)$ is maximal, i.e. n_0 is such that

$$d_{n_0}(\mathbf{x}_N^*) = d(\mathbf{x}_N^*)$$

The number of particles of the minimum-energy configuration \mathbf{x}_N^* inside the sphere S_{n_0} is

$$d(\mathbf{x}_N^*)\text{Vol}(S_{n_0}) = n_0^3 d(\mathbf{x}_N^*)\text{Vol}(S_1)$$

Consider now the $\bar{\Omega}_n(\ell) = \bar{\Omega}_1(\ell)n^3$ elementary cubes which surely cover S_n . Then one of them must contain a number of particles of the configuration \mathbf{x}_N^* at least

$$\left\lceil \frac{d(\mathbf{x}_N^*)\text{Vol}(S_{n_0})}{\bar{\Omega}_{n_0}(\ell)} \right\rceil = \left\lceil \frac{d(\mathbf{x}_N^*)\text{Vol}(S_1)}{\bar{\Omega}_1(\ell)} \right\rceil \geq \left\lceil \frac{c_0 W_a^+(\mathbf{x}_N^*)}{\bar{\Omega}_1(\ell)} \right\rceil$$

where in the last inequality we use Proposition 3. \square

Proposition 4 *Let \mathbf{x}_N^* be a minimum-energy configuration. Let $\ell \leq 0.4275$ and $a \leq \frac{\sqrt{3}}{2}\ell$ then*

$$W_a^+(\mathbf{x}_N^*) \leq \max \left\{ \frac{V_a\left(\frac{\sqrt{6}}{2}\ell\right)}{\frac{c_0}{2\bar{\Omega}_1(\ell)} \left[V_a\left(\frac{\sqrt{6}}{2}\ell\right) + V_a\left(\sqrt{3}\ell\right) \right] - 1} ; \frac{V_a\left(\frac{\sqrt{3}}{2}\ell\right)}{\frac{c_0}{4\bar{\Omega}_1(\ell)} \left[V_a\left(\frac{\sqrt{3}}{2}\ell\right) + 3V_a\left(\frac{3}{2}\ell\right) \right] - 1} \right\}$$

Proof. In view of Proposition 3, given a minimum energy configuration \mathbf{x}_N^* , there exists an elementary cube Δ containing at least β particles among the \mathbf{x}_N^* . Let us subdivide Δ in eight subcubes of size $\ell/2$. Let us consider the pairs of such subcubes whose intersection is just one vertex (opposite pairs). There are two cases to be considered.

1. There is a pair of opposite subcubes such that each subcube of this pair contains at least one particle.

2. In any pair of opposite cubes at least one subcube of the pair contains no particle so that all particles are contained in at most 4 subcubes.

Case 1. Let us assume that there is a pair of opposite subcubes of the cube Δ each one containing (at least) a particle. Take two spheres of radius $\sqrt{6}\ell/2$ centered in these two particles. By a simple geometric argument it is easy to see that these two spheres cover the whole cube Δ . This cube Δ contains β particles, thus there is at least a particle, say in position x_h^* , in one of the two opposite subcubes, such that at least $\beta_1 \geq \beta/2$ particles of the minimum-energy configuration are at distance less or equal to $\sqrt{6}\ell/2$ from x_h^* . Let us denote by Σ the sphere of radius $\sqrt{6}\ell/2$ centered at x_h^* . Then, for any particle x_i^* of the minimum-energy configuration we have

$$|x_h^* - x_i^*| \leq \begin{cases} \frac{\sqrt{6}\ell}{2} & \text{if } x_i^* \in \Sigma \cap \Delta \\ \sqrt{3}\ell & \text{otherwise} \end{cases}$$

Remember now that the condition (3.4) for ℓ is such that $V_a(\sqrt{3}\ell)$ is positive. Moreover since by hypothesis $a \leq (\sqrt{3}/2)\ell$, we can bound the positive part $W_a^+(h, \mathbf{x}_N^*)$ of the interaction of the particle x_h^* with all other particles in the minimum-energy configuration as

$$\begin{aligned} W_a^+(h, \mathbf{x}_N^*) &= \sum_{\substack{j \in \mathbf{I}_N : j \neq h \\ |x_h^* - x_j^*| < 2^{-1/6}}} V_a(|x_h^* - x_j^*|) \geq (\beta_1 - 1)V_a(\sqrt{6}\ell/2) + (\beta - \beta_1)V_a(\sqrt{3}\ell) \geq \\ &\geq (\beta/2 - 1)V_a(\sqrt{6}\ell/2) + (\beta/2)V_a(\sqrt{3}\ell) \end{aligned}$$

Hence we obtain

$$W_a^+(\mathbf{x}_N^*) \geq \frac{\beta}{2} \left[V_a(\sqrt{6}\ell/2) + V_a(\sqrt{3}\ell) \right] - V_a(\sqrt{6}\ell/2)$$

Recalling now the definition of β we get

$$W_a^+(\mathbf{x}_N^*) \geq c_0 \frac{W_a^+(\mathbf{x}_N^*)}{2|\bar{\Omega}_1(\ell)|} \left[V_a(\sqrt{6}\ell/2) + V_a(\sqrt{3}\ell) \right] - V_a(\sqrt{6}\ell/2)$$

whence

$$W_a^+(\mathbf{x}_N^*) \left[\frac{c_0}{2|\bar{\Omega}_1(\ell)|} \left[V_a(\sqrt{6}\ell/2) + V_a(\sqrt{3}\ell) \right] - 1 \right] \leq V_a(\sqrt{6}\ell/2)$$

We now have to choose ℓ in such way that the l.h.s. of the inequality above is positive. That is, we must impose that

$$\frac{c_0}{2|\bar{\Omega}_1(\ell)|} \left[V_a(\sqrt{6}\ell/2) + V_a(\sqrt{3}\ell) \right] > 1$$

i.e., recalling the definitions (3.3) and (3.5) of c_0 and of $\bar{\Omega}_1(\ell)$ resp. we get the condition

$$\frac{\frac{23}{32}}{2\left(\frac{4}{\ell}\right)^3} \left[\frac{1}{(\sqrt{6}\ell/2)^{12}} - \frac{2}{(\sqrt{6}\ell/2)^6} + \frac{1}{(\sqrt{3}\ell)^{12}} - \frac{2}{(\sqrt{3}\ell)^6} \right] > 1$$

i.e.

$$\frac{23}{2^{12}} \left[\frac{2^6 + 1}{3^6} \ell^{-9} - \frac{2}{3} \ell^{-3} \right] - 1 > 0 \tag{3.7}$$

Let us call ℓ_1 the value of ℓ such that the l.h.s. of inequality above is equal to zero. Then one can check that $\ell_1 > 0.4275$ and hence (3.7) is satisfied by taking e.g.

$$\ell \leq 0.4275 \quad (3.8)$$

In conclusion, if ℓ satisfies (3.8) and Case 1 happens, we get that

$$W_a^+(\mathbf{x}_N^*) \leq \frac{\frac{2^6}{3^6 \ell^{12}} - \frac{2^4}{3^3 \ell^6}}{\frac{23}{2^{12}} \left[\frac{2^6+1}{3^6 \ell^9} - \frac{2}{3 \ell^3} \right] - 1}$$

Note that the function on the r.h.s. restricted to the interval $(0, \ell_1)$ is positive and goes to infinity as $\ell \rightarrow 0$ or $\ell \rightarrow \ell_1$ and therefore has a minimum at some point in the interval $(0, \ell_1)$. By computation one can check that this minimum occurs at a value slightly greater than $\ell = 0.3672$ where the function takes the value (slightly less than) 4712

Case 2. If Case 2 happens then all the β particles in the elementary cube Δ lie inside four of the eight subcubes.

In that case there is a subcube containing at least $\beta_1 \geq \beta/4$ particles. Choose any particle in this subcube, say the one at position x_h^* , then the remaining $\beta_1 - 1$ particles inside the subcube are all at distance less or equal $\sqrt{3}\ell/2$ from x_h^* (recall: the subcube has size $\ell/2$). The $\beta - \beta_1$ particles which are outside the subcube and inside the elementary cube Δ are, in the present Case 2, all contained in a parallelepiped of size $\ell \times \ell \times \ell/2$ which also contains x_h^* and thus they are at distance at most $3\ell/2$ from x_h^* . Therefore we can bound as before

$$\begin{aligned} W_a^+(h, \mathbf{x}_N^*) &= \sum_{\substack{j \in I_N: j \neq h \\ |x_h^* - x_j^*| < 2^{-1/6}}} V_a(|x_h^* - x_j^*|) \geq (\beta_1 - 1)V_a(\sqrt{3}\ell/2) + (\beta - \beta_1)V_a(3\ell/2) \geq \\ &\geq (\beta/4 - 1)V_a(\sqrt{3}\ell/2) + (3\beta/4)V_a(3\ell/2) \end{aligned}$$

Hence we obtain

$$W_a^+(\mathbf{x}_N^*) \geq \frac{\beta}{4} \left[V_a(\sqrt{3}\ell/2) + 3V_a(3\ell/2) \right] - V_a(\sqrt{3}\ell/2)$$

Proceeding as before we now get the inequality

$$W_a^+(\mathbf{x}_N^*) \left[\frac{c_0}{4|\bar{\Omega}_1(\ell)|} \left[V_a(\sqrt{3}\ell/2) + 3V_a(3\ell/2) \right] - 1 \right] \leq V_a(\sqrt{3}\ell/2)$$

So in Case 2 we must impose that

$$\frac{c_0}{4|\bar{\Omega}_1(\ell)|} \left[V_a(\sqrt{3}\ell/2) + 3V_a(3\ell/2) \right] > 1$$

and we get the condition

$$\frac{\frac{23}{32}}{4\left(\frac{4}{\ell}\right)^3} \left[\frac{1}{(\sqrt{3}\ell/2)^{12}} - \frac{2}{(\sqrt{3}\ell/2)^6} + \frac{3}{(3\ell/2)^{12}} - \frac{6}{(3\ell/2)^6} \right] > 1$$

i.e.

$$\frac{23}{2^6} \left[\left(\frac{6^5 + 2^5}{3^{11} \ell^9} \right) - \left(\frac{3^2 + 1}{3^5 \ell^3} \right) \right] - 1 > 0$$

Let us call ℓ_2 the value of ℓ such that the l.h.s. of inequality above is equal to zero. Then one can check that $\ell_2 \geq 0.6268$ and hence inequality above is widely satisfied if one continues to take

$$\ell \leq \ell_1 < 0.4275 \quad (3.9)$$

In conclusion, if ℓ satisfies (3.9) and Case 2 happens, we get that

$$W_a^+(\mathbf{x}_N^*) \leq \frac{\frac{2^{12}}{3^6 \ell^{12}} - \frac{2^7}{3^3 \ell^6}}{\frac{23}{2^6} \left[\left(\frac{6^5 + 2^5}{3^{11} \ell^9} \right) - \left(\frac{3^2 + 1}{3^5 \ell^3} \right) \right] - 1}$$

Note that the the function on the r.h.s. restricted to the interval $(0, \ell_2)$ is positive and goes to infinity as $\ell \rightarrow 0$ or $\ell \rightarrow \ell_2$ and therefore has a minimum at some point in the interval $(0, \ell_2)$. By computation one can check that this minimum occurs for (slightly greater than) $\ell = 0.5385$ where the function takes the value (slightly less than) 3020.

Therefore we have obtained that

$$W_a^+(\mathbf{x}_N^*) \leq F(\ell)$$

where ℓ can be any number in the interval $(0, \ell_1)$ and $F(\ell)$ is the function

$$F(\ell) = \max \left\{ \frac{\frac{2^6}{3^6 \ell^{12}} - \frac{2^4}{3^3 \ell^6}}{\frac{23}{2^{12}} \left[\frac{2^6 + 1}{3^6 \ell^9} - \frac{2}{3 \ell^3} \right] - 1} ; \frac{\frac{2^{12}}{3^6 \ell^{12}} - \frac{2^7}{3^3 \ell^6}}{\frac{23}{2^6} \left[\left(\frac{6^5 + 2^5}{3^{11} \ell^9} \right) - \left(\frac{3^2 + 1}{3^5 \ell^3} \right) \right] - 1} \right\}$$

Note that by the discussion above $F(\ell)$ restricted to the interval $(0, \ell_1)$ is positive and goes to infinity as $\ell \rightarrow 0$ or $\ell \rightarrow \ell_1$ and therefore $F(\ell)$ has a minimum in some place in the interval $(0, \ell_1)$. However, in order to optimize the bound on the convergence radius, it is convenient to choose an $\ell \in (0, \ell_1)$ as large as possible (in such way as to maximize a). By computation one can check that by taking e.g. $\ell = 0.42$ the function $F(\ell)$ takes the value (slightly less than) 15545. \square

Theorem 4 *If $a = 0.3637$, then the cutoffed Lennard-Jones potential $V_a(|x|)$ defined in (2.14) is such that the minimal distance r_{min}^a at which particles in a minimum energy configuration admits the following lower bound*

$$r_{min} \geq 0.44$$

Proof. Choosing $\ell = 0.42$, by Proposition 5, if $a = 0.3637 < \frac{\sqrt{3}}{2}(0.42)$ we have that, in any minimum-energy configuration \mathbf{x}_N^*

$$W_a^+(\mathbf{x}_N^*) \leq F(\ell = 0.42) < 15545$$

Since $V_a(r_{min}) \leq W_a^+(\mathbf{x}_N^*)$ we obtain

$$V_a(r_{min}) < 15545$$

which yields at least $r_{min} \geq 0.446$. \square

We can now conclude the proof of Lemma 1. The cut-off Lennard-Jones potential $V_a(|x|)$ with $a = 0.3637$ is such that the minimal distance r_{min}^a between pairs of particles in a minimum-energy configuration is greater than 0.44. It is easy to see that this immediately implies that $V_a(|x|)$ is stable (see e.g. [5], Sec. 4.2). Moreover $r_{min}^a > a$. This implies that the stability constant of $V_a(|x|)$ is equal to the stability constant of the whole Lennard-Jones potential $V_{LJ}(|x|)$ (since the two potentials coincide for distances greater than a). Indeed, any x_1^*, \dots, x_N^* which is a minimum-energy configuration for V_a , since $V_{LJ}(|x|) \geq V_a(|x|)$ for all $|x| \leq r_{min}^a$ and $V_{LJ}(|x|) = V_a(|x|)$ for all $|x| > r_{min}^a$, is also a minimum-energy configuration for V . Viceversa, since for the whole Lennard-Jones potential $V(|x|)$ the minimal distance r_{min} between pairs of particles in a minimum-energy configuration is also such that $r_{min} > a$ (see e.g. the recent bounds for $r_{min} \geq 0.67985$ obtained in [19]), any x_1^*, \dots, x_N^* which is a minimum-energy configuration for $V_{LJ}(|x|)$ is also a minimum-energy configuration for $V_a(|x|)$ (since $V_a(|x|) = V_{LJ}(|x|)$ for $|x| \geq r_{min} > a$).

3.1 Conclusions

The reasoning developed in this note for the specific case of the Lennard-Jones pair potential (2.12) could be easily generalized for a physically relevant class of non-absolutely integrable pair potentials, namely the so called Lennard-Jones type pair potentials. We recall that a pair potential $V(|x|)$ is of Lennard-Jones type if there exist $r_0 > 0$ and $\varepsilon > 0$ such that:

$$V(|x|) \geq \frac{C_1}{|x|^{3+\varepsilon}} \text{ for } |x| \leq r_0, \quad |V(|x|)| \leq \frac{C_2}{|x|^{3+\varepsilon}} \text{ for } |x| > r_0$$

Indeed, Propositions 1, 3 and 4 are clearly true also for a potential $V(|x|)$ of Lennard-Jones type. On the other hand Proposition 2 holds for a potential $V(|x|)$ of Lennard-Jones type only if $\varepsilon > 1$.

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